CHAPTER - VII
ANALYSIS OF HEAVY METALS
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7.1 Introduction

Heavy metals in water sources, especially in ground water need to be investigated as they find entry into different matrices-water, soil and biomass. The aquatic systems receive these heavy metals directly or indirectly from point sources or non-point sources. Many sources of water are now contaminated with heavy metals that have adverse effect on health of a living being. Heavy metals are formed naturally as a product of weathering and disintegration of rocks. They cannot be degraded or destroyed. The entry of heavy metals into human and living systems is via food, drinking water and air. Though the metabolism of human body needs some of these elements in trace amounts, they are a danger as they tend to bio-accumulate and lead to poisoning.

During the early investigations of heavy metals in water sources, Huff (1948) investigated Cu, Pb, Cd and Zn from Colorado river surface while Turekian and Kleinkopf assessed Cu, Mn, Pb, Ti and Cr in mine surface waters. Most of the early investigations deal with metal contamination of ground-water, their transport mechanisms and impact on ground water (Amadi, et al., 1989, Inglis et al., 1986; Mackay and Cherry, 1989; Suarez, 1989; Zaporozec, 1982).

Although there are more than 100 elements in the periodic table, only 80 of the these are metals and of these 80 metals, only about 18 metals are toxic (Khokpar, 1993). The metals cadmium (Cd), Chromium (Cr), Copper (Cu), Boron (B), Iron (Fe), Mercury (Hg), Lead (Pb), Nickel (Ni), Manganese (Mn), Molybdenum (Mo), Vanadium (V) and Zinc (Zn) are referred to as heavy metals. Copper, lead, cadmium, chromium, zinc have the potential to become carcinogens (Sundarman et al., 1977) and mutagens (Deminatti, 1979).
The activities of man and his interference with nature along with the need of growth in food production, resulting in the necessity of using chemicals and fertilizers, discharge of sewage and industrial effluents and indiscriminate growth of technologies have resulted in the heavy metals finding their way into the natural systems. William et al., (1974) have made a list of the sources of heavy metals. A few important sources of metal pollutants are the electroplating industry, paint industry, auto-exhaust emissions, pesticides and fertilizers, nuclear reactors etc.

Heavy metals enter the human system through diet via the route of phytoplankton, zooplankton and fishes. They can also enter the food chain through plants.

Heavy metals are highly toxic and persistent because of which they are high risk pollutants. It is therefore necessary to keep track of the changing concentration of these metals and their compounds in different environmental segments for good environmental management. Veena et al (1997) indicate that the concentration of heavy metals in the environment increased due to both anthropogenic activities and natural processes. The concentration level of heavy metals increase as they are transported by water and gather in water bodies and sediments after they are discharged by industrial and domestic effluents. The sediments are found to have a high concentration of these elements. They can be considered as ‘chemical archives’ of heavy metal depositions which provide a lot of information to resolve the source and sink of heavy metal pollution (Cundy et al., 2003). Jha et al., (2003) have studied the modes of transportation and levels in sediments and soils to understand the environmental problems arising from contaminated materials.

The present study has investigated the presence of heavy metals cadmium, chromium, copper, iron and zinc in Kharghab river water in each of the nine places.
7.2 Experimental Procedure

Water samples were collected early in the morning in the first week of every month from each site of the nine towns selected for study in pre-cleaned and acid–washed plastic one litre bottles and transported immediately to the laboratory in ice-box to avoid contamination.

7.2.1 Cadmium - Colourimetric method

Principle

Cadmium ions react with dithizone to form a pink-red coloured complex which can be determined colourimetrically after extraction with chloroform.

Procedure

A portion of filtered sample (digested to measure total cadmium by the method followed for chromium determination) containing 1to 10µg Cd was taken in a separating funnel. The pH of digested sample was adjusted by adding 6N NaOH using thymol blue indicator. The colour change at the end point (pH 2.8) was from blue to yellow.

The volume of sample adjusted to 25 cm$^3$ with distilled water was added with 1cm$^3$ sodium potassium tartarate, 5cm$^3$NaOH-KCN solution (400g NaOH + 10g KCN in 1 litre), 1cm$^3$ hydroxylamine hydrochloride solution and 15cm$^3$ stock dithizone solution (100mg/L) in sequence.

The contents were shaken with CHCl$_3$ and the lower layer of CHCl$_3$ was transferred into another separating funnel containing 25cm$^3$ of cold tartaric acid. 10cm$^3$moreCHCl$_3$ were added to the first funnel, shaken well and drained into the second funnel. The transfer was done very fast (as cadmium dithizonate decomposes on prolonged contact with NaOH having CHCl$_3$).

The CHCl$_3$ lower layer was discarded after shaking the funnel for about 2 minutes. Then 5cm$^3$ of pure CHCl$_3$ were added, shaken and the lower layer discarded, such that all the cadmium was retained in the tartaric acid solution.
To the above solution, 0.25cm³ of hydroxylamine hydrochloride solution (20g/100ml), 15cm³ standard dithizone solution (1mg/1L) and 5cm³ NaOH–KCN solution (400g NaOH+ 0.5g KCN per litre ) in sequence were added, shaken and allowed to settle into 2 layers. The lower layer of CHCl₃ was taken by filtration and the colour developed was measured at 518 nm.

The standard curve was obtained using standard solutions (0, 2, 4,6,8& 10 µg Cd solution in a series of separating funnels and adjusting the volume to 25 cm³ with distilled water) which were prepared following the same procedure as for the sample to develop the colour.

Calculation :-

\[
\text{Total Cd, mg/L} = \frac{Ax100}{(B \times C)}
\]

\[
\text{Dissolved Cd, mg/L} = \frac{A}{\text{Volume of sample}}
\]

Where,

A= µgCd from standard curve
B= cm³ original sample digested
C= cm³ portion from 100cm³ total digest

7.2.2 Chromium - Colorimetric method

Principle

Dissolved hexavalent chromium forms a compound of red-violet colour when reacted with diphenylcarbazide solution in acid medium. Total (dissolved + particulate) chromium can be obtained after digestion of sample with H₂SO₄ and HNO₃ acid mixture. The total dissolved chromium is determined by conversion of trivalent chromium to hexavalent chromium by oxidation with
potassium permanganate. Excess potassium permanganate is then destroyed by sodium azide ($\text{NaN}_2$).

Although this reaction is highly specific to chromium, Mo, Hg, Va may interfere with the analysis. The concentration of Hg and Mo can be tolerated upto 200mg/L. Vanadium should not be present more than 10 times to the that of chromium concentration.

**Procedure**

The volume of sample taken for analysis of chromium depended on the concentration of heavy metals as given in Table 7.1.

**Table 7.1: The volume of sample digested having different concentration of heavy metals**

<table>
<thead>
<tr>
<th>Concentration mg /L</th>
<th>Volume of sample in cm$^3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>&lt;1</td>
<td>-</td>
</tr>
<tr>
<td>1-10</td>
<td>1000</td>
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<td>10-100</td>
<td>100</td>
</tr>
<tr>
<td>100-1000</td>
<td>10</td>
</tr>
</tbody>
</table>

**For determination of total chromium**

Suitable volume of water sample was taken in an evaporating dish and acidified with concentrated sulphuric acid using methyl orange indicator. 5cm$^3$ of concentrated nitric acid and 2cm$^3$ of 30% hydrogen peroxide were added. The sample was evaporated to 15-20cm$^3$ on a heater.

The contents were then transferred to a conical flask and added with 5cm$^3$ of conc. HNO$_3$ and 10cm$^3$ of conc. H$_2$SO$_4$ acids. Evaporated again till white fumes of SO$_2$ just appeared. The contents were cooled, the volume made upto 50cm$^3$ was heated to boiling and filtered with 2 to 3 washings of the filter.
paper with distilled water. The final volume was made upto 100cm$^3$ in a volumetric flask.

From the digested solution, a portion was taken (containing 10-100µg Cr) and added with a few drops of methyl orange. The solution was made just basic with addition of and ammonium hydroxide.

Drop wise addition of H$_2$SO$_4$ (1:1) was done until the solution became just acidic. A further 1cm$^3$ of acid was added in excess. Next KMnO$_4$ solution was added till a persistent pink colour was obtained. A few drops were added in excess.

The solution was boiled for 2 minutes. Then 1cm$^3$ of NaN$_2$ solution was added and boiling continued. Addition of NaN$_2$ solution and boiling was carried out till the red colour faded away. The solution was boiled for further 1 minute, after the red colour disappeared.

The contents were cooled, five drops of conc. H$_3$PO$_4$ acid were added and diluted to 100cm$^3$. 2cm$^3$ of diphenylcarbazide solution were added and kept aside for 5 to 10 minutes for the red violet colour to develop fully.

The intensity of the colour was measured at 540 nm. The intensity of the colour in the sample solution (a measure of Cr concentration) was compared against a standard curve. The standard curve was prepared in the range of 10 to 100 µg Cr by taking 2 to 20cm$^3$ of standard chromium solution (5µg/cm$^3$) added with 1 cm$^3$ of H$_2$SO$_4$ (1:1) solution and made upto 100cm$^3$. 2cm$^3$ of diphenylcarbazide were added to develop the colour and absorbance reading were recorded at 540nm

(b) Determination of dissolved Cr (VI) only

A portion of filtered sample was taken (having 10-100µg Cr$^{6+}$) and colour was developed as in the case of standard curve preparation
Calculation

Total Cr, mg/L = \( \frac{A \times 100}{B \times C} \)

Total dissolved Cr, mg/L = \( \frac{A}{\text{Volume of sample}} \)

A = µg Cr from standard curve
B = cm\(^3\) original sample digested
C = cm\(^3\) portion from 100 cm\(^3\) of total digest.

7.2.3 Copper : Colorimetric method

Principle

Copper sulphate forms a blue colour complex (Cupra ammonium sulphate) when treated with aqueous ammonium hydroxide solution. The intensity of the blue colour of the complex depends on the concentration of copper sulphate in the solution.

Procedure

Standard solution of copper sulphate was prepared as stock solution. An intense blue colour was developed by adding 10% ammonium hydroxide to the solution to various concentrations of copper sulphate solution in the range 0.002 mg/L to 2.0 mg/L. The absorbance of the solutions was measured at 600 nm and a calibrated chart was prepared. The water samples were also similarly treated and absorbance recorded. The concentration of copper was obtained from the calibrated chart.

7.2.4 Iron : Colourimetric method

Principle

Iron is converted into ferrous state by boiling with HCl acid and hydroxylamine solution. The reduced iron chelates with 1, 10- Phenanthroline
at pH-3.2 to 3.3 to form an orange–red coloured complex. The intensity of this
colour is proportional to concentration of the iron in the sample and hence can
be determined colorimetrically based on Beer’s law.

The boiling of the sample initially with an acid removes cyanide, nitrite
and polyphosphate interference while addition of hydroxylamine removes the
interference of strong oxidizing agents. Excess of phenanthroline is used to
avoid errors caused by precipitation ofphenanthroline by bismuth, cadmium,
mercury, silver and other metals.

**Procedure**

50 cm$^3$ of the sample containing not more than 4 mg/L of iron were taken
in a 150 cm$^3$ conical flask. To this, 2 cm$^3$ of HCl acid and 1 cm$^3$ of
hydroxylamine solution were added and the contents were boiled to half the
volume for complete dissolution of all the iron.

The treated solution was cooled and 10 cm$^3$ of ammonium acetate buffer
with 2 cm$^3$ of phenanthroline solution were added when an orange-red colour
appeared (excess phenanthroline was added to account for interference from
other heavy metals).

The volume was made upto 100 cm$^3$. After 10 minutes, the absorbance
of the solution was recorded on a spectrophotometer using 510 nm filter. The
standard curve for comparison was charted in the range of 1 to 4 mg/L of iron
using various dilutions of standard iron solution. The concentration of Fe was
calculated directly from the standard curve.

**7.2.5 Zinc : Zincon method**

**Principle:**

Zinc is determined spectrophotometrically by conversion into blue
coloured complex with 2 – carboxy 2’-hydroxyl- 5’suphoformazyl benzene
(Zincon) solution buffered at pH-9.
As many other heavy metals also complex with zincon, all the metals are first converted into cyanide complex by the addition of chloral hydrate.

**Procedure**

To determine soluble zinc, the sample was filtered and for total Zinc, 1 cm$^3$ of conc. HCl was added to 50 cm$^3$ of sample, filtered and pH adjusted to 7 with 6N NaOH.

10 cm$^3$ of the sample, (with not more than 70 µg Zn) were taken in conical flask. Then 0.5g sodium ascorbate, 1.0 cm$^3$ KCN solution, 5.0 cm$^3$ buffer solution (NaOH+ Na$_3$BO$_3$) and 3.0 cm$^3$ zincon reagent were added in sequence, mixing thoroughly after each addition. 3 cm$^3$ of chloral hydrate solution were added and the intensity of the colour was measured exactly after five minutes at 620nm.

The standard curve in the range of 0 to 70 µg Zn (0, 2.5, 5, 10, 30, 50, 70 µg Zn) was prepared by taking suitable volumes of standard zinc solution (10 µg Zn) and making then upto 10.0 cm$^3$. The intensity of the colour developed for each solution was recorded following the same procedure for developing colour as for the sample.

**Calculation**

\[
\text{Zn, mg/L} = \frac{\text{µg of Zn}}{\text{cm}^3 \text{ of sample}}
\]

**7.3 Results and Discussion**

**7.3.1 Cadmium**

The cadmium ion concentration in natural waters is strongly controlled by pH and oxidation potential. It is known to be a non-essential and non-beneficial element with a high toxic potential (Train, 1979). The main source of cadmium is the cladding industry. Cadmium is a cumulative poison which can
reside in the body for more than ten years (Khopkar, 1993). It affects the liver, pancreas and kidney. The permissible limit of cadmium is 0.003mg/L (WHO, 2004).

In the present study it is observed that cadmium concentration was more than the permissible limit in all the nine places studied in some of the months. However, in most months the presence of cadmium was not detectable.

The monthly variation of cadmium in the nine towns is depicted in Fig 7.1 and Fig 7.2. The seasonal average values are shown in Table 7.2 and graphically represented in Fig 7.3.

It is seen that in Ahmadabad, the cadmium concentration is zero in most of the months while it is more than the permissible limits in the months of January 2012 (0.02±0.02 mg/L), May 2012, (0.06±0.002 mg/L) and August 2012 (0.05±0.014 mg/L). The seasonal average values indicate that the rainy season had the maximum value of 0.02±0.02 mg/L where as in winter season the average value was 0.012±0.018mg/L.

Arasur showed zero presence in rainy season but was present on an average to an extent of 0.02 and 0.0033 ±0.0057mg/L during summer and winter seasons respectively. In the monthly observations cadmium was present in the water samples during the months of November 2011 (0.03mg/L), February 2012 (0.01mg/L) and July 2012 (0.061mg/L). These values are higher than the permissible limits.

In Ghaemabad, cadmium presence was found in the month of October 2011, (0.001mg/L), November 2011 (0.0033 mg/L),February 2012 (0.055 mg/L), May 2012 (0.042 mg/L) and June 2012 (0.06 mg/L). Except for October and November 2011, the cadmium concentration was found to exceed the desirable limit. During the remaining months presence of cadmium was not detected. Seasonally, the average was highest during the rainy season at 0.037 (± 0.035) mg/L and least during the winter season (0.013±0.015 mg/L).
The monthly variation (Fig 7.2) of cadmium in Khampich showed that the maximum value of 0.035 (± 0.016) mg/L was observed in the month of March 2012 while May 2012 showed a value of 0.02 (±0.007 mg/L) and September 2012 had a value of 0.01 (± 0.005) mg/L. The least value was detected in the month of November 2011 (0.0024 ± 0.001 mg/L). Seasonally, the summer season showed no presence of cadmium, winter season had a presence of 0.0013 (± 0.0012) mg/L and rainy season showed a value of 0.018 (± 0.017) mg/L.

In Khonsar, excepting for the months of November 2011 (0.03± 0.009 mg/L), February 2012 (0.01± 0.005 mg/L) and June 2012 (0.04 ± 0.01 mg/L) in all the other months cadmium could not be detected. Seasonally, the average value was the highest during the summer season at 0.013 (± 0.004 mg/L) while no cadmium was detected in rainy season and 0.003 (± 0.0057) mg/L was detected in winter season.

In the 12 month period in Malga, the concentration of cadmium was highest in the month of August 2012 at a concentration of 0.13 (± 0.008) mg/L which is very much higher than the desirable limit of 0.003 mg/L. In most months cadmium was not detected. Season wise, all the three seasons showed almost the same value (about 0.043 ± 0.023 to 0.046 ± 0.045 mg/L).

In Qudejan, the cadmium presence was detected only in the month of December 2011 at 0.01 mg/L. All other months showed zero presence. Seasonally too, rainy and summer seasons showed no presence while winter season had an average presence of 0.003 (±0.005) mg/L.

The summer season showed no presence of cadmium in Rahmatabad where as winter season (0.013 ± 0.021 mg/L) and rainy season (0.0153 ± 0.026) mg/L had almost equal concentration. Month wise the highest presence was in the month of September 2012 at 0.048 (± 0.002 mg/L). Excepting for Jan 2012 (0.038 ± 0.02 mg/L) and March 2012 (0.046 ± 0.001 mg/L) all other months did not show cadmium presence.
In Wist, cadmium was present in the water samples of only two months, March 2012 (0.094 ± 0.003 mg/L) and August 2012 (0.042 ± 0.02 mg/L). No presence of cadmium was found during the winter season, while the summer average was 0.014 (± 0.024) mg/L and rainy season average was 0.031 (± 0.0524) mg/L.

The cadmium concentration is found to be higher than the permissible limit in most of the sites during the twelve month period of study. However there is no presence of cadmium in some of the months at all sites. This variation is due to the variational ativities during different months of the people settled near the site points which include fishing (boat spoilage, paint fallout) and small scale industrial effluents.

**Fig 7.1:** Monthly variation of Cadmium between period 2011-12 in Ahmadabad, Arasur, Ghaemabad, Khampich, Khonsar

**Fig 7.2:** Monthly variation of Cadmium between period 2011-12 in Malga, Qudejan, Rahmatbad, Wist
Table 7.2 Average Seasonal Variation of Cadmium (mg/L)

<table>
<thead>
<tr>
<th></th>
<th>Ahmadabad</th>
<th>Arasur</th>
<th>Ghaemabad</th>
<th>Khampich</th>
<th>Khonsar</th>
<th>Malga</th>
<th>Qudejan</th>
<th>Rahmatbad</th>
<th>Wist</th>
</tr>
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<tbody>
<tr>
<td>Winter av</td>
<td>0.01</td>
<td>0.00</td>
<td>0.02</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.01</td>
<td>0.00</td>
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<tr>
<td>Winter sd</td>
<td>0.01</td>
<td>0.01</td>
<td>0.03</td>
<td>0.00</td>
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</tr>
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<td>0.00</td>
<td>0.03</td>
<td>0.05</td>
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<tr>
<td>Summer av</td>
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<td>0.02</td>
<td>0.02</td>
<td>0.00</td>
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<td>0.04</td>
<td>0.00</td>
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</tr>
<tr>
<td>Summer sd</td>
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<td>0.03</td>
<td>0.00</td>
<td>0.02</td>
<td>0.08</td>
<td>0.00</td>
<td>0.00</td>
<td>0.02</td>
</tr>
</tbody>
</table>

Fig 7.3: Average seasonal variation of Cadmium
7.3.2 Chromium

Of the group VI elements, Cr is the most toxic metal. However, Cr (III) is not as toxic as Cr (VI). Chromium is mainly sourced from paint industry, glass industry, tanneries waste etc. The permissible limit of Cr is 0.05 mg/L (WHO, 2004). The presence of Cr can adversely affects aquatic life. It can cause dermatitis, chest trouble and lung cancer. In the range of 5mg/L, it is carcinogenic to animals (Sahu, 1991).

The monthly variation of chromium is given in Fig 7.4 and Fig 7.5. The average seasonal values are given in Table 7.3 and depicted in Fig. 7.6.

The chromium content was generally found to be less than the desirable limit of 0.05mg/L in most months of all the places. However, the values exceeded the desirable limit in some of the months of some places.

In Ahmadabad, excepting for the month of November 2011 (0.071±0.015mg/L), all other months showed less than 0.05mg/L to no presence. Season wise the winter average was maximum at 0.011 (±0.02)mg/L while both summer and rainy season averages were 0.0083 (± 0.0057)mg/L.

During the twelve month period studied, Arasur showed a value of 0.067 (± 0.003)mg/L in the month of January 2012, 0.065 (± 0.01) mg/L in October 2011 and 0.031 (± 0.012) mg/L in April 2012. All other months had zero concentration. The season average was highest during winter at 0.022 (± 0.038) mg/L and least during summer (0.0 ± 0.0) mg/L.

Ghaemabad monthly samples showed zero to less than the desirable limit concentration except for November 2011 (0.061±0.007 mg/L). Concentration in January 2012 was 0.03 ± 0.005 mg/L and Feb in 2012, 0.01 ± 0.009 mg/L. The winter season average was 0.013 (± 0.015) mg/L while summer and rainy season averages were 0.003 (± 0.052) mg/L and 0.002 (±0.003) mg/L.
Khampich showed monthly variations which were all less than 0.05 mg/L the desirable limit. A few months showed zero presence of chromium. The chromium concentration varied from a minimum value of 0.01 (± 0.005) mg/L during February 2012 to a maximum of 0.024 (± 0.01) mg/L in the month of December 2011. In few of the months (October 2011, January 2012, March 2012, May 2012 and June 2012) no chromium presence was detected. Season wise, rainy season had the least concentration (0.0043 ± 0.0075)mg/L while winter had the highest concentration at 0.011 (± 0.012)mg/L.

In Khonsar, excepting for October 2011 (0.003 ± 0.0015mg/L) and March 2012 (0.002 ± 0.00)mg/L, all other months had no presence of chromium. Seasonally, winter and summer periods had zero averages while the rainy seasonal average was 0.0066 ± 0.0011 mg/L.

Malga water sample showed chromium presence in most of the months with the highest concentration detected in November 2011 at 0.092(±0.012) mg/L. followed by August 2012 with 0.07 (± 0.018) mg/L. The least concentration was in March 2012 at 0.01 (± 0.002) mg/L. The winter average was 0.047 (± 0.023) mg/L and summer average was 0.023 (± 0.04) mg/L.

In Qudejan, chromium content was found only in the month of December 2011 (0.01 ± 0.001 mg/L). The rest of the months had zero concentration. Only winter season had an average of 0.0033 (± 0.0057) mg/L.

The chromium concentration in Rahmatabad ranged from 0.025(± 0.014) mg/L in July 2012 to 0.061 (± 0.02) mg/L in December 2011. Many months had zero concentration of chromium. Season wise averages were 0.020 ± 0.035 mg/L winter, 0.01 ± 0.017 mg/L in rainy and 0.024 ± 0.023 mg/L in summer seasons.

In Wist, a very high average value of 0.3 (± 0.5) mg/L was detected in winter while rainy season had an average value of 0.033 (± 0.057) mg/L and summer season average was zero. Monthwise most months showed zero
concentration while January 2012 had the highest content at 0.9 (± 0.008) mg/L.

Chromium concentration has the permissible limit of 0.05mg/L (WHO). In the present study, the concentration of chromium ranged from well below the permissible limit in most of the months at all the sites to a little above the permissible limit in some of the months in some of the sites. The variation and excess concentration of chromium are due to effluents from nearby small scale industries, like plating industry, discharge of chemicals such as dyes and paints, utilized by people in their businesses of carpet making, cloth weaving etc.

Fig 7.4: Monthly variation of Chromium between period 2011-12 in Ahmadabad, Arasur, Ghaemabad, Khampich, Khonsar

Fig 7.5: Monthly variation of Chromium between period 2011-12 in Malga, Qudejan, Rahmatbad, Wist
<table>
<thead>
<tr>
<th></th>
<th>Ahmadabad</th>
<th>Arasur</th>
<th>Ghaemabad</th>
<th>Khampich</th>
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<th>Qudejan</th>
<th>Rahmatbad</th>
<th>Wist</th>
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<tbody>
<tr>
<td>Winter av</td>
<td>0.01</td>
<td>0.02</td>
<td>0.01</td>
<td>0.01</td>
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<td>0.05</td>
<td>0.00</td>
<td>0.02</td>
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<tr>
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<td>0.02</td>
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</tr>
</tbody>
</table>

Fig 7.6: Average seasonal variation of Chromium
7.3.3 Copper

The desirable limit of copper in drinking water according to WHO is 0.05 to 2mg/L. Copper is an essential metal, necessary for enzyme activity in living systems in trace amounts. At higher concentrations, it can become toxic and it gives an undesirable taste to water. However copper deficiency can cause anemia, growth inhibition and loss of hair pigment. In the range of 5-15mg/L it is harmless to many aquatic species (Dwivedi and Tiwari, 1997).

Figures 7.7 and 7.8 give the monthly variations of copper in the nine places while Fig 7.9 depicts the seasonal variations with the values given in Table 7.4.

The copper content was negligible in the monthly water samples of Ahmadabad being in the range of 0.01 (± 0.0072)mg/L to 0.015 (± 0.011) mg/L. Excepting for November 2011, January 2012 and August 2012, all the other months showed no presence of copper in the water samples. The season averages were found to be 0.0033 (± 0.0057) mg/L in winter and 0.005 (± 0.0086) mg/L in summer. Rainy season average was zero.

Arasur had a range of 0.012 (±0.012) mg/L to 0.098 (±0.004) mg/L in the twelve month period studied. The maximum was in November 2011 (0.098±0.018 mg/L) and the least was in September 2012 (0.012 ± 0.009 mg/L). Many months had no copper presence. Seasonally, the winter average was zero, with rainy average being 0.006 ± 0.010mg/L and the summer average being 0.0043 ± 0.0075 mg/L.

In Ghaemabad there was no copper detected in the water samples in the months of December 2011, May 2012, July 2012 and August 2012. The maximum concentration of copper detected was 0.05 (± 0.014) mg/L in June 2012 and least value was in October 2011 and April 2011. The maximum seasonal average was determined in winter at 0.026 (± 0.023) mg/L. The least was in the rainy season showing a value of 0.01 (± 0.01)mg/L.
The desirable limit of copper being 0.05 – 2mg/L, Khampich had a range of copper content which was below this desirable range. The maximum value was 0.024 (± 0.009)mg/L in the month of December 2011 and the least was in the month of February 2012 (0.01± 0.01)mg/L. The winter average was 0.014 (± 0.012) mg/L while that of rainy season was higher at 0.035 (± 0.031)mg/L and the summer season average was 0.0036 (± 0.0063) mg/L.

The average seasonal variation of copper in Khonsar was found to be zero in summer, 0.01 (± 0.017)mg/L in rainy and 0.026 (± 0.046)mg/L in winter season. The month of December 2011 showed the highest value of 0.08 (±0.012) mg/L with October 2011 showing the least value at 0.011 (± 0.007) mg/L.

Malga monthly water samples exhibited a copper concentration range of 0.08 (±0.02) mg/L to 0.024 (±0.004) mg/L in five of the 12 month period. The rest of the months showed less than detectable concentration. Season wise, rainy season had 0.033 (± 0.041) mg/L, winter season had 0.004 (± 0.0069) mg/L and summer had an average of 0.008 (± 0.013) mg/L.

In Qudejan except for the month of January 2012 (0.013±0.002) mg/L, April 2012 (0.024±0.0091)mg/L and August 2012 (0.012±0.002) mg/L, all the other months had no copper. An average of 0.0043 (± 0.0075) mg/L in winter, 0.008 (± 0.013) mg/L in rainy and 0.004 (± 0.0069)mg/L in summer were found in the three seasonal periods.

In Rahmatabad, seasonal averages were seen to be almost same in the winter (0.026±0.046 mg/L) and rainy (0.024±0.042 mg/L) seasons. Summer season had an average of 0.043(±0.045) mg/L. In the monthly variations, the highest value of copper recorded was 0.09 (±0.012) mg/L in June 2012 and least value was 0.04 (±0.002) mg/L in August 2012. Many months did not show any copper content.

The months of January 2012 (0.085±0.006) mg/L, June 2012 (0.15±0.07) mg/L and July 2012 (0.13±0.0045 mg/L) only showed copper
content. The rest of months had less than detectable values. Season wise, the winter average was the least at 0.028 (±0.049) mg/L while that of summer was the highest at 0.093 (±0.081) mg/L. The rainy season had no copper content.

Copper concentration between different sites showed a narrow range of variation. The copper content was found to be in the range of negligible concentration to below the desirable limit. Season wise too, some of sites showed copper presence in only some of the seasons. Such seasonal variations in the copper distribution is due to discharge of domestic wastes, industrial effluent disposal and to the various small scale business activities of people settled close to the site.

![Fig 7.7: Monthly variation of Copper between period 2011-12 in Ahmadabad, Arasur, Ghaemabad, Khampich, Khonsar](image1)

![Fig 7.8: Monthly variation of Copper between period 2011-12 in Malga, Qudejan, Rahmatbad, Wist](image2)
### Table 7.4 Average Seasonal Variation of Copper (mg/L)

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**Fig 7.9: Average seasonal variation of Copper**
7.3.4 Iron

In drinking water, the permissible limit of iron is 0.3 to 1.0 mg/L. Higher concentration of iron imparts bitter taste and stinky flavor (Khursid et al. 1997). The presence of iron in water increases the hazard of pathogenic organisms which require iron for their growth.

The monthly variations are depicted in Fig 7.10 and Fig 7.11. The seasonal average values given in Table 7.5 and depicted graphically in Fig 7.12. The iron content was found to be less than permissible limit in all the places in all the months.

In Ahmadabad, the iron content varied from a minimum value of 0.08 (± 0.025) mg/L in November 2011 to a maximum of 0.13 (± 0.003) mg/L in June 2012 with many months showing no presence of iron. Season averages were zero in winter, 0.03 (± 0.063) mg/L in rainy and 0.08 (± 0.07) mg/L in summer.

In Arasur, the iron concentration varied from 0.033(±0.028) mg/L in July 2012 to 0.09(±0.01) mg/L in February 2012. The values were 0.06 (±0.021) mg/l in October 2011 and 0.075 (±0.033) mg/L in May 2012. All the other months had less than detectable quantities. Seasonally, winter season had the maximum concentration with an average of 0.03 (±0.052) mg/L and summer had the least with 0.011(±0.011) mg/L.

Ghaemabad exhibited a monthly iron range of 0.012±0.01 mg/L (August 2012) to a maximum of 0.066 (±0.023) mg/L (February 2012). In six of the months no iron content was detected. The seasonal average was highest in the winter season at 0.033(±0.033) mg/L with the least value being seen in summer season at 0.004 (± 0.0069) mg/L.

In Khampich the monthly variation ranged from 0.01±0.008 mg/L in November 2011 to a high of 0.05±0.014 mg/L in May 2012 and 0.05±0.007 mg/L in July 2012. In few of the months no iron content was detected. An
average of 0.0036 (±0.0063) mg/L in winter season, 0.026 (± 0.025) mg/L in rainy season and 0.017 ± 0.029 mg/L in summer season were recorded. The monthly average was 0.0225 (± 0.0269 ) mg / L.

In Khonsar, the monthly iron average was 0.01 (± 0.023) mg/L. The maximum value was 0.08 (±0.006) mg/L in December 2011 while the least was in October 2011 (0.011±0.01 mg/L). Seasonal average values showed no presence of iron in winter and summer seasons while rainy season had an average value of 0.0167± 0.029 mg/L.

The seasonal variation of iron in Malga showed that summer season had the highest value at 0.233(±0.404) mg/L while it was least in rainy season (0.17±0.29 mg/L).

Monthly average at Qudejan was 0.03±0.045 mg/L. Excepting for 4 months, the rest of the months showed zero presence of iron. The maximum value recorded was 0.093(±0.008) mg/L in the month of February 2012. The least monthly value was 0.088 (± 0.042) mg/L in August 2012.

In Rahmatabad the monthly values ranged from 0.017 (± 0.005) mg/L in July 2012 to a value of 0.08 (± 0.021) mg/L in February 2012. The monthly average was 0.021(±0.03) mg/L. Season wise the winter average was 0.026(±0.046) mg/L, rainy seasonal average was 0.0187(±0.032) mg/L and summer average was 0.005(±0.009) mg/L.

The seasonal averages of iron in rainy and summer seasons were zero for Wist. The winter average was found to be 0.021mg/L. The monthly average was 0.0075(±0.019) mg/L. Iron was detected only in the months of February 2012 (0.064 ±0.0047 mg/L) and September 2012 (0.026±0.022 mg/L).

The presence of iron in trace amounts is necessary for animals and plants. It is combined with oxygen to transport blood in vertebrates. The major sources of iron pollution in environment especially in water bodies are due to
weathering of rocks, from soil, from discharge of effluents of steel factories and metal manufacturing plants and corrosion of pipes.

The iron values in the present study, are observed to be below the permissible limit (WHO). The variation in iron concentration between months and seasons of a place are due to the discharge of industrial effluents and chemicals utilized by the inhabiting people in their work of trade.

Fig 7.10: Monthly variation of Iron between period 2011-12 in Ahmadabad, Arasur, Ghaemabad, Khampich, Khonsar

7.11: Monthly variation of Iron between period 2011-12 in Malga, Qudejan, Rahmatbad, Wist
Table 7.5 Average Seasonal Variation of Iron (mg/L)

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<th>Ghaemabad</th>
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Fig 7.12: Average seasonal variation of Iron
7.3.5 Zinc

The main source of Zinc is galvanization and alloy industries. The permissible limit of zinc is 5mg/L (WHO, 2004). Zinc is an essential element, necessary for various enzyme reactions in living systems. However, it can become toxic above the 5mg/L limit not only to human systems but also to plants (Hewitt, 1948). Zinc causes chills, nausea, vomiting and metal fume fever (Khopkar, 1993). Zinc in excess can cause a number of environmental problems though it is an essential element in human and animal nutrition. The major sources of Zinc into environment are discharge of domestic waste water, coal burning and metal manufacture to name a few factors.

The monthly variations are depicted in Fig 7.13 and Fig 7.14. The seasonal average values are given in Table 7.6 and also depicted graphically in Fig 7.15.

In the present study the concentration of Zinc was well below the permissible limit of 5mg/L in all the nine places studied.

In Ahmadabad, it ranged from 0.03 (±0.02) mg/L to a maximum of 0.16 (±0.08) mg/L over the 12 month period. The monthly average of zinc was 0.055 (± 0.060) mg/L. In the months of Jan 2012, March 2012, June 2012 and August 2012, no zinc presence was detected. The winter average was 0.063 (±0.055) mg/L while that of rainy season was 0.06 (± 0.079) mg/L and summer was 0.026 (± 0.046) mg/L.

The monthly average of zinc concentration in Arasur was 0.043(±0.060) mg/L. Zinc content was highest in the month of August 2012 (0.15±0.09 mg/L). The least value recorded (0.02 ± 0.04 mg/L) was in the month of December 2011. Some months showed zero concentration. Seasonwise summer average was maximum at 0.093(±0.081) mg/L. The winter average (0.01±0.01 mg/L) was lesser than rainy season average (0.067±0.056 mg/L).
Ghaemabad had seasonal zinc averages of 0.016±0.014 mg/L in winter, 0.010 ±0.017 mg/L in rainy and 0.035±0.030 mg/L in summer seasons. The monthly average was 0.020(±0.020) mg/L. The highest value of 0.054 (±0.032) mg/L was recorded in August 2012 while the least value was in February 2012 (0.023±0.021mg/L).

The Khampich town had an average value of 0.0186±0.027 mg/L over the 12 month period of study. The maximum value of zinc was 0.07 (±0.02) mg/L in December 2011 with the least value recorded in month of March 2012 (0.02± 0.014 mg/L). The season wise variation showed a winter average of 0.004 (± 0.006) mg/L, a rainy season average of 0.026 (± 0.025) mg/L and a summer season average of 0.017 (± 0.029) mg/L.

In Khonsar, the maximum value of zinc content was recorded in November 2011 (0.33±0.12) mg/L and the least value in July 2012 (0.04±0.022) mg/L. The monthly average was 0.05 (±0.096) mg/L. Many months showed zero concentration. The winter season average was 0.04(±0.036) mg/L while that of rainy season was 0.037 (±0.032) mg/L and summer season average was 0.013(±0.023) mg/L.

Malga had a seasonal average variation of 0.2(±0.46 ) mg/L in winter, 0.42(± 0.37) mg/L in rainy and 0.17 (±0.29) mg/L in summer. The monthly average over the twelve month period was 0.34±0.34 mg/L. The highest concentration of zinc was recorded in October 2011 at 0.91(±0.14) mg/L . The value of 0.8(±0.2) mg/L, 0.65 (± 0.15) mg/L, 0.62(±0.12) mg/L, 0.51(±0.22) mg/L and 0.6 (± 0.3) mg/L were recorded in few of the months. The rest of the months showed zero concentration.

Qudejan had a monthly zinc average of 0.074 (±0.05) mg/L with the highest recorded value being 0.28 (±0.008) mg/L in October 2011. There was no zinc presence in the months of November 2011, January 2012, February 2012 and June 2012. The least value was recorded in May 2012 at 0.05
(±0.041) mg/L. The season average of 0.05(±0.08) mg/L in winter, 0.08
(± 0.03)mg/L in rainy and 0.045 (± 0.042)mg/L in summer were observed.

In Rahmatabad, the seasonal averages were 0.04(±0.035) mg/L in
winter, 0.017(±0.029) mg/L in rainy and 0.003(±0.006) mg/L in summer
seasons. The monthly average was 0.018 (±0.027) mg/L. The highest value was
0.063 (±0.028) mg/L in month of February 2012 and least was 0.011(±0.009)
mg/L in July 2012. In seven of the months there was no zinc presence.

The town of Wist showed zero presence of zinc in the summer season, a
maximum value of 0.065±0.056 mg/L in rainy season and 0.014±0.025 mg/L in
winter season. The monthly average was 0.0198(±0.04) mg/L. Except for
December 2011 (0.043±0.015 mg/L), March 2012 (0.095±0.021 mg/L) and
May 2012 (0.1±0.11 mg/L), the other months had no zinc presence.

The permissible limit of zinc in drinking water being 5 mg/l, it is
observed that the zinc concentration in all the nine places was well below this
limit. However, variations between months and seasonal averages at each place
would be due to mixing of domestic discharges and anthropogenic sources into
the river water.

The concentration of most of the heavy metals studied are mostly within
the permissible limits though they were not uniform between months and
seasons.In the present study, cadmium is found to be on the higher side of the
permissible limit .Addition of heavy metals into the river water are due to
discharge of domestic sewage ,small scale industrial effluents and agricultural
run-offs .The spoilage of ships and paints from boats and fishing activities also
increase the concentration of heavy metals such as lead,zinc and cadmium in
the river water (Wargen,1981, Ramesh Babu and Selvanayagam, 2013)
**Fig 7.13:** Monthly variation of Zinc between period 2011-12 in Ahmadabad, Arasur, Ghaemabad, Khampich, Khonsar

**Fig 7.14:** Monthly variation of Zinc between period 2011-12 in Malga, Qudejan, Rahmatbad, Wist
## Tables 7.6 Average Seasonal Variation of Zinc (mg/L)

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**Fig 7.15: Average seasonal variation of Zinc**